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(54) **Solid polyaminoester polymers, their production and use.**

(57) Solid polyaminoester polymers containing units of acrylic acid ester monomer having an average acrylate functionality of at least 2.5 and of aliphatic amine monomer having a number average molecular weight of at most 1000, an average amine hydrogen functionality of at least 3 and an amine hydrogen equivalent weight of less than about 100, the equivalent ratio of acrylate to amine hydrogen being 0.5 to 2.0 in order to provide new polymers useful as thermoset plastics and moldable by reaction injection molding or liquid injection molding processes.

They may be prepared by introducing a monomer mixture containing the acrylate monomer and the amine monomer into a mold and allowing the mixture to react.

EP 0 002 457 A1

Solid Polyaminoester Polymers, Their Production and Use

This invention is concerned with solid polyaminoester polymers, their production and use. The polymers of the
5 invention are useful as thermoset plastics.

The technical field to which the invention relates is the production of molded plastics articles by reaction injection molding ("RIM") or liquid injection molding ("LIM") processes wherein a liquid reaction mixture is
10 introduced into a mold, especially a closed injection mold, and is rapidly polymerized to a rigid thermoset plastic.

The only plastics previously used successfully in the RIM or LIM processes have been low modulus, low deflection temperature under flexural load (DTUFL) polyurethanes; no
15 one has ever suggested polyaminoesters which are prepared from amines and acrylates for these processes. Polyaminoesters have previously been suggested mainly for coatings (U.S. Patent 3,845,056); coatings and films (U.S. Patent 2,759,913), or gel-like products.

20 There is a need for high modulus, high DTUFL plastics moldable by the RIM or LIM process.

This invention provides solid polyaminoester polymer containing units of acrylic acid ester monomer having an average acrylate functionality of at least 2.5 and of
25 aliphatic amine monomer having a number average molecular weight of at most 1000, an average amine hydrogen functionality of at least 3 and an amine hydrogen equivalent weight of less than about 100, the equivalent ratio of acrylate to amine hydrogen being 0.5 to 2.0.

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It is an advantage of the compositions of the invention that the polymers can be made quickly and efficiently in a mold at low temperatures and pressures and have an excellent balance of properties.

5 Preferred polymers are molded polymers having the composition defined above. The acrylate monomer and aliphatic amine react rapidly via a Michael-type reaction, either primarily or exclusively, to a final rigid thermo-

10 set polymer product having a high softening temperature. The acrylate monomer can be the product of partial or total acrylation of triols, tetrols, or higher polyols, or mixtures of these tri- and higher functional acrylates with diacrylates and may of course be a mixture of indi-
vidual monomers. Examples of suitable tri- and higher
15 functional acrylates are trimethylolpropane triacrylate, pentaerythritol tetraacrylate or triacrylate, glycerol triacrylate, and the like. Diacrylates which can be used in admixture therewith include 2,2-dimethylpropylene glycol diacrylate, ethylene glycol diacrylate and the
20 like. These acrylates are preferably all liquid at or near room temperature. Methacrylates are not suitable.

In the case of the low molecular weight aliphatic amines, by "aliphatic" is meant amines whose nitrogen is attached to an aliphatic carbon, but this is not meant
25 to exclude amines which also contain aromatic or cycloaliphatic moieties. The low molecular weight amine monomer preferably has a number average molecular weight below 600. The equivalent weight of the aliphatic amines is preferably below about 100. For example, ethylene
30 diamine, diethylenetriamine, triethylene tetramine, tetraethylene pentamine, propylenediamine, polyethyleneimine, diaminoethane, aminoethylpiperazine, 1,4-(diaminomethyl)cyclohexane, and m-xylylenediamine are suitable, either individually or in admixture with each other or with
35 other aliphatic amines. The preferred amines are of the formula $H_2N(CH_2CH_2NH)_nH$ wherein n is 1 to 4. The amines or mixtures thereof are preferably liquids at or near room temperatures.

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Optionally, small amounts of free radical initiator can be used in the process for making the polymers of the invention. Suitable initiators are generally of the peroxide or azo class such as those normally used for
5 free radical polymerization. For example, di-t-butyl peroxide, azo isobutyryl nitrile, and the like can be used in amounts of about 0.01 to 0.5 percent by weight based on reactants. When the initiator is used it causes free radical polymerization of the excess acrylate.

10 When no initiator is used, the preferred acrylate to amine hydrogen equivalents ratio is about 0.5 to 1.09. When the initiator option is followed, the preferred acrylate to amine hydrogen equivalents ratio is about 0.8 to 2.0.

15 Optionally, one or more ethylenically unsaturated monomers other than acrylates, which are copolymerizable with acrylates but are less reactive with amines than are the acrylates in the composition, can be included in amounts less than 50% by weight. For example, styrene
20 and methyl methacrylate can be used in such minor amounts, most preferably less than about 15% by weight based on reactants. When these other ethylenically unsaturated monomers are used, the initiator should also be used. When these other monomers are used, they copolymerize
25 with the excess acrylate groups.

The compositions and articles produced have a wide variety of end uses, including electrical insulator parts, distributor caps, gears, fenders, boat hulls, foams, and sheet, due to their excellent balance of properties,
30 especially with regard to their rapid moldability, their rigidity and their high use temperature, and their hardness. For some end uses it is preferable to incorporate additives such as glass or asbestos fiber reinforcement, inert particulate filler, dyes, pigments, UV light and
35 other stabilizers, flame retardants, mold release agents. Suitable amounts of glass or other fibrous reinforcement are about 5 to 50% by weight. Suitable amounts of inert particulate filler are about 5 to 75% by weight.

In accordance with the process aspect of this invention, the acrylate monomer, the amine monomer, optionally the ethylenically unsaturated monomer other than acrylate and free radical initiator, and the optional additives are mixed and introduced to a mold, preferably a closed mold, and allowed to react preferably for 1 to 2000 seconds at a mold temperature of 0 to 200°C, more preferably 20 to 120°C. The preferred molding system is a closed mold, usually an injection mold. Only very low pressures and temperatures are required, usually only 20 psi and 50°C, to quickly mold the high softening temperature articles of the invention, contrary to normal thermoplastic injection molding which requires high temperatures, usually 200-300°C, and pressures, usually 10,000 to 50,000 psi, because of the high viscosity of the polymer melt. With other thermoset systems, high pressures and temperatures are needed because of the viscosity and reaction temperatures of those materials. No solvents are needed, and preferably none is used in the process.

Foams can also be made by the process by including in the polymerizable mixture low boiling inert solvent which boils under the reaction conditions so as to produce rigid foamed articles.

Some embodiments of the invention will now be described in the following Examples wherein all parts and percentages are by weight unless otherwise indicated.

The following procedures are used to measure the properties in the Examples:

ASTM D638 - tensile strength and modulus
 ASTM D790 - flexural strength and modulus
 ASTM D256 - notched Izod impact strength
 ASTM D648 - DTUFL (deflection temperature under flexural load)

ASTM D785 - Rockwell hardness
 ASTM D1525- Vicat softening point

The 10 mil deflection temperature test is similar to ASTM D1525. The Vicat apparatus is used but the measurement is begun at -20°C and run to 10 mil indentation.

Acrylate equivalent weights are measured by the pyridine sulfate dibromide technique:

trimethylolpropane triacrylate (TMPTA)	= 111
pentaerythritol triacrylate (PETA)	= 108
neopentylglycol diacrylate (NPGDA)	= 127
ethylene diacrylate, electrophoresis grade	= 87

Examples 1-9 illustrate the effect of acrylate-amine ratio on the gel time and properties of TMPTA-TEPA polyaminoesters.

Example 1

Tetraethylenepentamine (38.22 parts) and trimethylolpropane triacrylate (130.0 parts) are mixed with a glass stirring rod at room temperature. After the components are mixed for about 10 seconds, they form a homogeneous solution which becomes warm. The solution is then poured between two glass plates 0.4 cm. apart. The solution gels in two minutes. The sheet is removed from the mold after 10 minutes. It is postcured by heating to 180°C over a 2 hour period. The physical properties are summarized in Table 1. The polyaminoester shows less than 0.5% change in weight and dimensions during immersion in gasoline for 8 days.

Examples 2A - 9

Trimethylolpropane triacrylate - tetraethylene-pentamine polyaminoester sheets of various compositions are cast by the procedure in Example 1. The gel times and properties are listed in Table 1. At equivalent ratios less than 0.5, the tensile strength and modulus are too low for a useful plastic. At equivalent ratios greater than 2.0, as in comparative Example 9, the tensile strength and modulus is too low for a useful plastic and the gel times are too long for RIM processing.

TABLE 1

	<u>Example</u>	<u>Equivalents Ratio Acrylate/Amine</u>	<u>Gel Time (minutes)</u>	<u>Tensile Strength (psi)</u>
15	2A	0.54	<1	4700
	2B	0.64	<1	6600
	2C	0.74	1	8600
	2D	0.78	1	7400
20	1	0.83	2	7200
	2E	0.88	2	6900
	3	0.92	2	6300
	4	1.00	3	4100
25	5	1.08	4	2400
	6	1.3	10	
	7	1.6	25	
	8	1.9	90	
	9 comparative	2.2	150	

TABLE 1 continued

	<u>Tensile Modulus (psi)</u>	<u>DTUFL At 264 psi (°C)</u>	<u>Vicat (°C)</u>	<u>Rockwell Hardness</u>
5	140,000	50	150	M50
	290,000	50	180	M50
	360,000	50	190	M50
	360,000	50	210	M50
	330,000	50	210	M40
10	340,000	50	210	M30
	300,000	40	210	M30
	190,000	40	210	M0
	95,000	40	210	M0
	75,000			
15	40,000			
	20,000			
	<10,000			

Examples 1, 10, and 11 illustrate the effect of
 20 reaction temperature on mold time.

Example 10

The procedure of Example 1 is repeated with the
 exception that the reagents are equilibrated at 0°C before
 they are mixed. Gelation requires 5 minutes and the
 25 sheet is removed from the mold in 25 minutes.

Example 11

When the reagents are equilibrated at 50°C before they
 are mixed, gelation occurs in less than one minute and the
 sheet is removed from the mold in 5 minutes.

30 The properties of the plastics described in the above
 two Examples are essentially identical to the properties of
 the plastic as described in Example 1.

Examples 12 - 24 illustrate the effect of amine
 structure, acrylate structure, and component ratio.

35 Example 12 - TMPTA-DETA Polyaminoester

Diethylenetriamine (22 parts) and trimethylolpropane
 triacrylate (110 parts) are reacted at 0°C as described in

Example 1. Properties are listed in Table 2.

Example 13 - TMPTA-EDA Polyaminoester

Ethylenediamine (16.49 parts) and trimethylolpropane triacrylate (105.7 parts) are reacted at 0°C as described in Example 1. Properties are listed in Table 2.

Example 14 - TMPTA-XDA Polyaminoester

m-Xylylenediamine (34.1 parts) and trimethylolpropane triacrylate (105.8 parts) are reacted at 25°C as described in Example 1. Properties are reported in Table 2.

Example 14A - TMPTA-DAMC Polyaminoester

1,3-(Diaminomethyl)cyclohexane (30.5 parts) and trimethylolpropane triacrylate (91.4 parts) are reacted at 25°C as described in Example 1. Properties are reported in Table 2.

Example 14B - TMPTA-PEI Polyaminoester

This Example illustrates use of amines of higher molecular weight in the invention.

Polyethyleneimine (4.3 parts) and trimethylolpropane triacrylate (13.8 parts) are reacted at 25°C as described in Example 1. Properties are reported in Table 2.

Examples 15 - 19 - PETA-XDA Polyaminoester

m-Xylylenediamine and pentaerythritol triacrylate in various ratios are reacted as in Example 1. The physical properties are shown in Table 2.

Example 20 - PETA-TEPA Polyaminoester

Tetraethylenepentamine and pentaerythritol triacrylate are reacted by the procedure of Example 1. The physical properties are shown in Table 2.

Examples 21 - 24 - PETA-PDA Polyaminoester

1,2-Diaminopropane and pentaerythritol triacrylate are reacted as in Example 1. The properties are shown in Table 2.

TABLE 2

	<u>Example</u>	<u>Acrylate</u>	<u>Amine</u>	<u>Equiv. ratio</u> <u>Acrylate/Amine</u>	<u>Gel time</u> <u>(Minutes)</u>
5	12	TMPTA	DETA	0.93	1 (0°C)
	13	TMPTA	EDA	0.87	1 (0°C)
	14	TMPTA	XDA	0.95	60
	15	PETA	XDA	0.72	0.5
	16	PETA	XDA	0.84	0.5
10	17	PETA	XDA	0.93	0.5
	18	PETA	XDA	1.01	1.0
	19	PETA	XDA	1.12	1.0
	20	PETA	TEPA	0.98	0.2
	21	PETA	PDA	0.70	0.3
15	22	PETA	PDA	0.82	0.5
	23	PETA	PDA	0.93	0.5
	24	PETA	PDA	1.06	0.5
	14A	TMPTA	DAMC	0.95	2
	14B	TMPTA	PEI	1.2	0.5

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TABLE 2 Continued

	Tensile Strength (psi)	Tensile Modulus (psi)	DTUFL at 264 psi (°C)	Vicat (°C)	Rockwell Hardness
	6,000	300,000	50	200	M40
5	5,400	270,000	40	200	M10
	8,400	400,000	60	240	M50
	-----	-----	90	---	---
	11,000	430,000	100	230	M90
	9,600	430,000	100	230	M90
10	-----	-----	100	---	---
	-----	-----	70	---	---
	-----	-----	65	---	---
	-----	-----	50	---	---
	6,900	510,000	70	---	M80
15	12,000	520,000	80	---	M80
	-----	-----	65	---	---
	-----	300,000	50	200	---
	-----	-----	50	200	---

Examples 25-33 offer a comparison of properties of polyaminoesters formed from dicarylates to properties of polyaminoesters formed from triacrylates. The flexural strength, modulus, and thermal behavior of diacrylate polyaminoesters are unacceptable for a useful plastic.

Examples 25-33

25 1,2-Propylenediamine is reacted with electrophoresis grade ethylene diacrylate in various ratios by the procedure of Example 1. The only exception is that post-cure is for 70 hours at 70°C. The properties measured are shown in Table 3.

30 Examples 28-29

1,2-Propylenediamine is reacted with trimethylolpropane triacrylate by the procedure of Examples 25-27. The properties are listed in Table 3.

Examples 30-33

35 Tetraethylenepentamine is reacted with neopentylglycol diacrylate (NPGDA) in various ratios and with

trimethylolpropane triacrylate by the procedure of Example 1. The properties are shown in Table 3.

TABLE 3

<u>Example</u>	<u>Acrylate</u>	<u>Amine</u>	<u>Equiv. ratio Acrylate/Amine</u>
25*	EDA	PDA	0.86
26*	EDA	PDA	0.93
27*	EDA	PDA	1.02
28	TMPTA	PDA	0.84
29	TMPTA	PDA	1.00
30*	NPGDA	TEPA	0.79
31*	NPGDA	TEPA	0.86
32*	NPGDA	TEPA	0.92
33	TMPTA	TEPA	0.82

* Comparative

TABLE 3 continued

	Flexural Strength (psi)	Flexural Modulus (psi)	10 Mil Penetration Temp. (°C)
	440	1,600	8
	390	1,300	8
	540	3,000	20
	13,600	300,000	165
	8,700	170,000	172
	290	2,400	-1
	260	2,800	-6
10	260	2,700	-1
	11,400	300,000	195

The comparison shown in the Examples in Table 3 demonstrates the importance of the acrylate functionality.

- 15 Comparative Examples 34-36 illustrate that methacrylates, aromatic amines, and compounds with two amine hydrogens are unreactive and, therefore, inappropriate to the invention.

Example 34 - (Comparative)

- 20 Ethylenediamine (2.66 parts) is reacted with trimethylolpropane trimethacrylate (16.85 parts) by the procedure of Example 1. This Example is comparative because of the methacrylate rather than acrylate. After 4 days at room temperature the solution is very viscous
- 25 but not gelled. All attempts to react these at higher temperatures lead only to soft gels, no plastic articles can be made.

Example 35 - (Comparative)

- 30 2,4-Diaminotoluene (2.73 parts) is mixed with trimethylolpropane triacrylate (10.0 parts) by the procedure of Example 1. The Example is comparative because of the aromaticity of the amine. The mixture is allowed to stand at 60°C for 16 hours. No increase in viscosity occurs. No plastic material can be made.

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Example 36 - (Comparative)

n-Butylamine (5.26 parts) is added to trimethylol-propane triacrylate (14.89 parts) as in Example 1. This Example is comparative because of the amine hydrogen
5 functionality. After 6 hours at room temperature the solution becomes viscous but gelation does not occur until 24 hours. No plastic material can be made from this combination of monomers - only rubbery gels.

Examples 37-65 illustrate the properties of poly-
10 aminoesters containing free radical initiator and unsaturated monomer.

Example 37

m-Xylylenediamine (40.63 parts) is added to a solution of 0.40 parts di-t-butyl peroxide in penta-
15 erythritol triacrylate (142.4 parts). The components are mixed with a glass rod and poured into the glass sheet mold. The polyaminoester is postcured by heating to 175°C over a 1 hour period. Properties are listed in Table 4.

20 Example 38

m-Xylylenediamine (34.5 parts) is added to a mixture of di-t-butyl peroxide (0.33 parts), styrene (13.8 parts), and pentaerythritol triacrylate (102.4 parts). The components are mixed with a glass rod and poured into a
25 sheet mold. The sheet is postcured by heating to 175°C over a 1 hour period. Its properties are shown in Table 4.

Examples 39-42

m-Xylylenediamine was added to a mixture of di-t-butyl peroxide, styrene, and pentaerythritol triacrylate
30 as in Example 38. Properties are listed in Table 4.

Examples 43-45 - PETA-XDA Polyaminoester with MMA and di-t-butyl peroxide

m-Xylylenediamine is added to a mixture of di-t-butyl peroxide, methyl methacrylate, and pentaerythritol tri-
35 acrylate as in Example 38. Properties are shown in Table 4.

Examples 46-57

Tetraethylenepentamine is reacted with a mixture of trimethylolpropane triacrylate, styrene, and di-t-butyl peroxide as in Example 38. The properties are shown in Table 5. These Examples illustrate the effect of component ratio. At ratios lower than 0.8 the addition of initiator with or without unsaturated monomer has negligible effect on the DTUFL. At very high ratios (2.0) the reaction is too slow and/or the exotherm is too high to be useful in RIM processing, also, the shrinkage would be too high for useful RIM processing. At intermediate levels, significant improvements in modulus, tensile strength, and DTUFL result by addition of initiator and unsaturated monomer.

Other amines are reacted with pentaerythritol triacrylate, styrene, and di-t-butyl peroxide as in Example 38. Properties are shown in Table 6. Styrene in excess of about 15% leads to cracking of the plastic.

Examples 66 and 67 illustrate the incorporation of filler and glass fiber.

Example 66

Tetraethylenepentamine (16.0 parts) is added to a mixture of calcium metasilicate (28.2 parts) in di-t-butyl peroxide (0.27 parts), styrene (9.5 parts), and pentaerythritol triacrylate (80.2 parts). The components are mixed with a glass stirring rod and poured into a glass sheet mold. The sheet is postcured by heating to 175°C over 1 hour. The plastic has a tensile modulus of 800,000 psi and a DTUFL at 264 psi of 195°C.

TABLE 4

	<u>Example</u>	<u>Acrylate</u>	<u>Amine</u>	<u>Equiv. ratio Acrylate/ Amine</u>	<u>Initiator</u>
5	37	PETA	XDA	1.12	---
	38	PETA	XDA	1.12	0.2%
	39	PETA	XDA	0.93	---
	40	PETA	XDA	0.93	0.2%
	41	PETA	XDA	0.93	0.2%
10	42	PETA	XDA	0.93	0.2%
	43	PETA	XDA	0.93	0.2%
	44	PETA	XDA	1.12	0.2%
	45	PETA	XDA	1.12	0.2%

TABLE 4 Continued

	<u>Monomer</u>	<u>Modulus (psi)</u>	<u>Tensile Strength (°C)</u>	<u>DTUFL at 264 psi (°C)</u>	<u>DTUFL at 66 psi (°C)</u>	<u>Rockwell Hardness</u>
5	----	470,000	14,900	70	80	M80
	----	470,000	11,900	145	200	M100
	----	430,000	9,600	95	-	M90
	6%S	430,000	9,100	110	-	M100
	8%S	430,000	7,900	125	190	M100
10	9%S	470,000	10,400	150	190	M105
	12%S	440,000	7,600	125	-	M100
	75MMA	480,000	11,500	149	190	M100
	95MMA	480,000	10,700	135	200	M100

TABLE 5

	<u>Example</u>	<u>Equiv. ratio Acrylate/ Amine</u>	<u>Initiator</u>	<u>Styrene %</u>
5	46	0.8	---	---
	47	0.8	0.2%	---
	48	0.8	0.2%	6%
	49	0.8	0.2%	9%
	50	1.1	---	---
10	51	1.1	0.2%	---
	52	1.1	0.2%	7%
	53	1.1	0.2%	9%
	54	1.3	---	---
	55	1.3	0.2%	---
15	56	1.3	0.2%	6%
	57	1.3	0.2%	8%

TABLE 5 Continued

	Modulus (psi)	Tensile Strength (psi)	DTUFL at 264 psi (°C)	DTUFL at 66 psi (°C)
5	350,000	7,000	50	---
	360,000	7,000	50	---
	370,000	8,500	50	---
	390,000	9,500	60	---
	95,000	3,000	45	45
10	350,000	10,000	50	180
	350,000	10,000	70	190
	325,000	9,800	80	190
	30,000	1,000	35	35
	330,000	10,300	110	195
15	340,000	9,500	95	200
	330,000	8,600	105	200

TABLE 6

<u>Example</u>		<u>Amine</u>	<u>Equiv. ratio Acrylate/ Amine</u>	<u>% Styrene</u>
5	58	PDA	1.05	6
	59	TEPA	0.86	9
	60		1.01	9
	61		1.17	9
	62		1.29	9
10	63	EDA	1.24	9
	64	1,3 PDA	1.27	9
	65	DETA	1.05	9

TABLE 6 Continued

	<u>Modulus</u> <u>(psi)</u>	<u>Flexural</u> <u>Strength</u> <u>(psi)</u>	<u>DTUFL</u> <u>at 264 psi</u> <u>(°C)</u>	<u>DTUFL</u> <u>at 66 psi</u> <u>(°C)</u>	<u>Rockwell</u> <u>Hardness</u>
5	480,000	12,500	145	175	M100
	400,000	6,400	120	---	M105
	---	---	150	---	M105
	470,000	5,800	167	200	M110
	---	---	170	---	M110
10	---	---	173	200	M105
	---	---	181	---	M110
	---	---	145	---	M105

Example 67

15 Tetraethylenepentamine (15.7 parts) is added to a mixture of glass fiber (25.9 parts) in di-t-butyl peroxide (0.29 parts), styrene (9.4 parts), and pentaerythritol triacrylate (78.4 parts). The components are mixed with a glass rod and poured into a 1.0 cm glass sheet mold. After

20 postcure the reinforced plastic has a DTUFL at 264 psi of 200°C and a flexural modulus of over 1,000,000 psi. The notched Izod impact strength of this material is 1.5 ft.-lb./in. compared to 0.25 ft.-lb./in. for the nonreinforced material.

25 Examples 68-71 describe the process as carried out in high speed production equipment.

Example 68

30 A 42. g shot of tetraethylenepentamine (1.0 part) and pentaerythritol triacrylate (2.5 parts) is metered and mixed in 1 second at 40°C in a Cincinnati Milicron RIM machine. The mixed material is fed directly into a closed electrical insulator mold. The insulator (8 cm x 2 cm x 2 cm) is removed from the mold after 30 seconds and post-cured. The Vicat softening point of this material was

35 200°C. The insulator was also very rigid, indicating utility at high load and temperature applications.

Example 69

The composition of Example 61 is processed by the procedure of Example 68. The connector is removed from the mold within one minute. After postcure the material has a Vicat softening point of 210°C and is also very rigid, indicating excellent use temperature and load bearing properties.

Example 70

A composition of tetraethylenepentamine (20 parts), di-t-butylperoxide (0.2 parts), styrene (9 parts), pentaerythritol triacrylate (70 parts) and milled glass (20 parts) are processed at 40°C in an Accuratio Systems, Inc. RIM processing Machine. The material (18 g) is delivered directly to a gear mold. The gear (5 cm in diameter and 1.5 cm long) is removed within 1 minute and postcured. The high modulus, good impact strength, and use temperature are good for this application.

Example 71

Example 70 is repeated with the exception that 100 parts calcium carbonate is substituted for the glass. The gear is removed from the mold within one minute.

Claims

1. Solid polyaminoester polymer containing units of acrylic acid ester monomer having an average acrylate
5 functionality of at least 2.5 and of aliphatic amine monomer having a number average molecular weight of at most 1000, an average amine hydrogen functionality of at least 3 and an amine hydrogen equivalent weight of less than about 100, the equivalent ratio of acrylate to amine
10 hydrogen being 0.5 to 2.0.
2. A polymer as claimed in claim 1 which is a molded polymer.
- 15 3. Polymer as claimed in claim 1 or 2 wherein the acrylic acid ester monomer is pentaerythritol triacrylate and/or trimethylolpropane triacrylate and the amine monomer is one or more of the monomers of the formula $H_2N(CH_2CH_2NH)_nH$ wherein n is 1 to 4.
20
4. A process for producing the polymer of any preceding claim which comprises introducing a monomer mixture containing the acrylate monomer and the amine monomer into a mold and allowing the mixture to react.
25
5. A process as claimed in claim 4 wherein the mixture is allowed to react for about 1 to 2000 sec and at a temperature of 0 to 200°C.
- 30 6. A process as claimed in claim 4 or 5 wherein said mold is a closed mold.
7. A process as claimed in claim 4, 5 or 6 wherein the temperature is 20 to 120°C.
35
8. A process as claimed in any of claims 4 to 7 which includes the further step of post curing the reaction product at 30 to 300°C for 1 to 22 hours.

9. A process as claimed in any of claims 4 to 8 wherein the reaction mixture also includes a free radical initiator and the equivalents ratio is 0.8 to 2.0.
- 5 10. A process as claimed in any of claims 4 to 8 wherein there is no free radical initiator present in the reaction mixture and the equivalents ratio is 0.5 to 1.09.

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European Patent
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EUROPEAN SEARCH REPORT

Application number

EP 78 10 1439

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p>US - A - 3 145 195 (KWAN CTSOU)</p> <p>* Claim 1 *</p> <p>-----</p>	1	<p>C 08 F 120/12</p> <p>C 08 G 73/00</p>
			<p>TECHNICAL FIELDS SEARCHED (Int. Cl.³)</p> <p>C 08 F 20/10-20/14-20/20-120/10-120/14-120/20</p> <p>C 08 G 73/00</p>
			<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant</p> <p>A: technological background</p> <p>O: non-written disclosure</p> <p>P: intermediate document</p> <p>T: theory or principle underlying the invention</p> <p>E: conflicting application</p> <p>D: document cited in the application</p> <p>L: citation for other reasons</p>
			<p>&: member of the same patent family, corresponding document</p>
<p><input checked="" type="checkbox"/> The present search report has been drawn up for all claims</p>			
Place of search		Date of completion of the search	Examiner
The Hague		15-02-1979	CAUWENBERG